2,5-Dimethoxy-3,4,6-trimethylbenzaldehyde

Ravindra Wickramasinhage, C. John McAdam* and Jim Simpson

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. *Correspondence e-mail: John.McAdam@otago.ac.nz

In the molecule of the title compound, $C_{12}H_{16}O_3$, the methyl and aldehyde substituents are disordered over four inversion-related C atoms on the benzene ring with an occupancy ratio of 0.75:0.25. The crystal structure features weak C—H···O hydrogen bonds and C—H···π contacts between a methoxy/methyl group and the benzene ring.

3D view

Chemical scheme
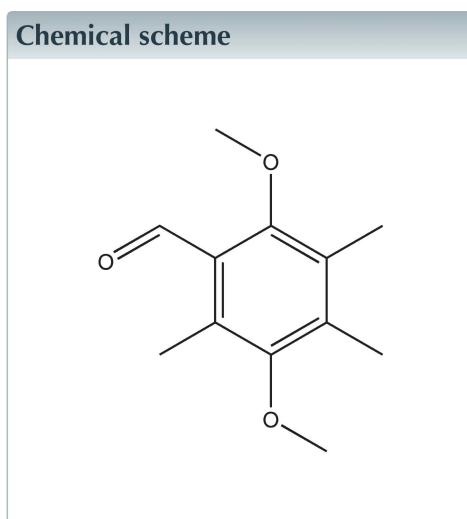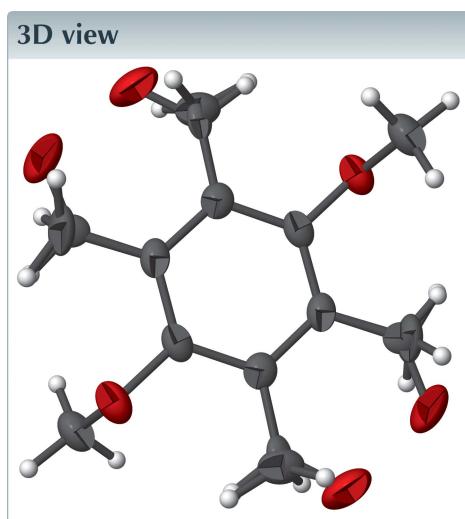
Structure description

The title compound, (I), was synthesized as a precursor to quinone-based electrochemical actuators as part of our ongoing research in this area (Goswami *et al.*, 2013). In the structure of (I), Fig. 1, which lies about an inversion centre situated at the centroid of the benzene ring, the methyl and aldehyde substituents are disordered on the C2 and C3 carbon atoms and their inversion equivalents in a 0.75:0.25 ratio, commensurate with the molecular formula $C_{12}H_{16}O_3$. The methoxy substituent on C1 is fully ordered. The non-hydrogen atoms of the methyl and aldehyde substituents lie close to the benzene ring plane while the methoxy groups are almost orthogonal to the ring with the dihedral angle between the C1–C3 and C1,O1,C11 planes being 87.15 (19)°. In the crystal weak C—H···O hydrogen bonds and C—H···π contacts, Table 1, stack the molecules along the *a*-axis direction, Fig. 2.

para-Dimethoxybenzenes with aldehyde substituents are not common, with only six unique examples in the Cambridge Structural Database (Version 5.37 Nov 2015 plus 1 update; Groom & Allen, 2014). These include the archetypal 2,5-dimethoxy-terephthaldehyde (Moorthy *et al.*, 2005; Nielsen *et al.* 2005; Kretz *et al.*, 2007) and an even closer relative of the title compound, 2,5-dimethoxy-3,6-dimethylterephthaldehyde (Moorthy *et al.*, 2005).
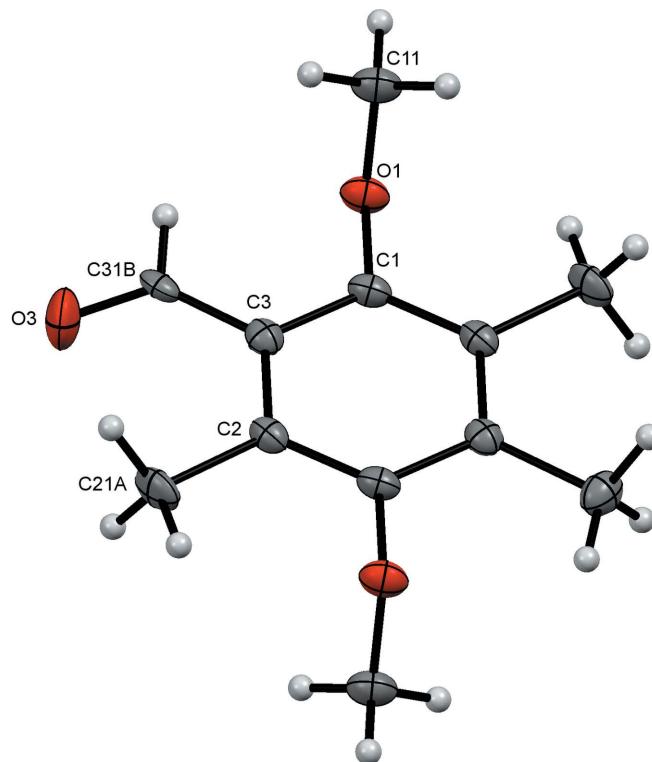
Figure 1
The structure of (I), showing the atom-numbering, with displacement ellipsoids drawn at the 50% probability level. Only one set of the disorder components is shown for clarity.

Synthesis and crystallization

2,5-Dimethoxy-3,4,6-trimethylbenzaldehyde was synthesized using a literature method (Häupler et al. et al., 2014). Colourles needle-like crystals were obtained from $EtOH/H_2O$ at ambient temperature.
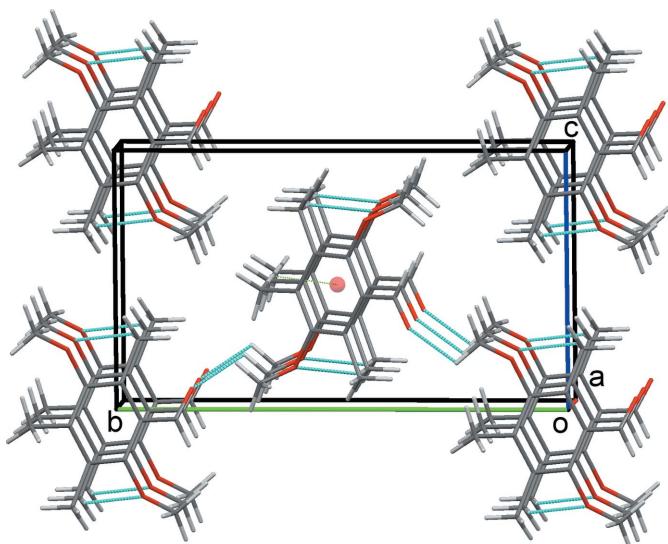

Figure 2
Crystal packing of (I) viewed along the a-axis direction. Only one set of the disorder components is shown for clarity. Hydrogen bonds are drawn as blue dashed lines and a representative $C—H\cdots\pi$ contact is drawn as a dotted green line with the ring centroid shown as a red sphere.

Table 1
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the C1–C3/C1^v–C3^v benzene ring.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C21A—H21C$\cdots$O1^i	0.98	2.66	3.506 (15)	144
C11—H11B$\cdots$O2^{ii}	0.98	2.71	3.195 (9)	111
C11—H11A$\cdots$O3^{iii}	0.98	2.42	2.788 (9)	102
C31A—H31C$\cdots$Cg1^i	0.98	2.71	3.48 (2)	138
C31A—H31C$\cdots$Cg1^{iv}	0.98	2.71	3.48 (2)	138

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 2$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 2, -y + 1, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C2 and C3 carbon atoms and their inversion opposites each carry disordered aldehyde and methyl substituents. Refining the disorder converged with occupancies of approximately 0.25 for the aldehyde and 0.75 for the methyl group, as would be expected with one aldehyde and three methyl substituents overall. The occupancies were therefore fixed at these values in the final refinement cycles.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{16}O_3$
M_r	208.25
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	4.5856 (3), 14.2281 (9), 8.3312 (4)
β (°)	98.515 (5)
V (Å^3)	537.57 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.75
Crystal size (mm)	$0.42 \times 0.13 \times 0.06$
Data collection	
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min}, T_{max}	0.719, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4051, 1068, 907
R_{int}	0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.623
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.186, 1.12
No. of reflections	1068
No. of parameters	103
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.24

Computer programs: CrysAlis PRO (Agilent, 2014), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), TITAN2000 (Hunter & Simpson, 1999), Mercury (Macrae et al., 2008), enCIFer (Allen et al., 2004), PLATON (Spek, 2009), publCIF (Westrip, 2010), WinGX (Farrugia, 2012).

References

Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Goswami, S. K., McAdam, C. J., Lee, A. M. M., Hanton, L. R. & Moratti, S. C. (2013). *J. Mater. Chem. A*, **1**, 3415–3420.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Häupler, B., Ignaszak, A., Janoschka, T., Jähnert, T., Hager, M. D. & Schubert, U. S. (2014). *Macromol. Chem. Phys.* **215**, 1250–1256.

Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.

Kretz, T. J. W., Bats, J. W., Lerner, H.-W. & Wagner, M. (2007). *Z. Naturforsch. Teil B*, **62**, 66–74.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Moorthy, J. N., Natarajan, R. & Venugopalan, P. (2005). *J. Mol. Struct.* **741**, 107–114.

Nielsen, C. B., Pittelkow, M. & Sørensen, H. O. (2005). *Acta Cryst.* E**61**, o473–o474.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

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Crystal data

$C_{12}H_{16}O_3$	$F(000) = 224$
$M_r = 208.25$	$D_x = 1.287$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 4.5856$ (3) Å	Cell parameters from 1932 reflections
$b = 14.2281$ (9) Å	$\theta = 6.1–72.2°$
$c = 8.3312$ (4) Å	$\mu = 0.75$ mm^{-1}
$\beta = 98.515$ (5)°	$T = 100$ K
$V = 537.57$ (6) Å^3	Needle, pale yellow
$Z = 2$	$0.42 \times 0.13 \times 0.06$ mm

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector	4051 measured reflections
	1068 independent reflections
Radiation source: SuperNova (Cu) X-ray Source	907 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.046$
Detector resolution: 5.1725 pixels mm^{-1}	$\theta_{max} = 73.8°$, $\theta_{min} = 6.2°$
ω scans	$h = -5\rightarrow5$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$k = -17\rightarrow17$
	$l = -10\rightarrow10$
$T_{min} = 0.719$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.065$	H-atom parameters constrained
$wR(F^2) = 0.186$	$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.4967P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	
1068 reflections	$(\Delta/\sigma)_{max} = 0.008$
103 parameters	$\Delta\rho_{max} = 0.22$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C11	0.6051 (6)	0.3451 (2)	0.8420 (3)	0.0435 (7)	
H11A	0.5783	0.2929	0.7644	0.065*	
H11B	0.5706	0.3229	0.9489	0.065*	
H11C	0.8067	0.3693	0.8495	0.065*	
O1	0.3988 (4)	0.41887 (13)	0.7878 (2)	0.0396 (5)	
C1	0.4525 (5)	0.45903 (17)	0.6431 (3)	0.0309 (6)	
C2	0.6504 (5)	0.53395 (17)	0.6492 (3)	0.0305 (6)	
C21A	0.804 (3)	0.5700 (11)	0.8144 (17)	0.047 (4)	0.75
H21A	0.7146	0.5403	0.9015	0.070*	0.75
H21B	0.7807	0.6383	0.8198	0.070*	0.75
H21C	1.0141	0.5542	0.8271	0.070*	0.75
C21B	0.794 (5)	0.568 (2)	0.796 (5)	0.026 (6)	0.25
H21D	0.7573	0.5343	0.8898	0.031*	0.25
O2	0.965 (3)	0.6353 (7)	0.8209 (11)	0.068 (3)	0.25
C3	0.6994 (5)	0.57594 (16)	0.5033 (3)	0.0307 (6)	
C31A	0.919 (4)	0.6577 (13)	0.4994 (19)	0.044 (4)	0.75
H31A	0.8575	0.7110	0.5609	0.065*	0.75
H31B	0.9226	0.6768	0.3867	0.065*	0.75
H31C	1.1164	0.6372	0.5480	0.065*	0.75
C31B	0.891 (11)	0.649 (3)	0.502 (3)	0.027 (6)	0.25
H31D	0.8952	0.6778	0.3992	0.033*	0.25
O3	1.053 (2)	0.6826 (7)	0.6122 (13)	0.063 (2)	0.25

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0497 (16)	0.0457 (15)	0.0356 (14)	0.0075 (12)	0.0077 (12)	0.0112 (11)
O1	0.0443 (10)	0.0467 (11)	0.0292 (9)	0.0074 (8)	0.0105 (7)	0.0074 (7)
C1	0.0317 (12)	0.0360 (13)	0.0252 (11)	0.0084 (9)	0.0053 (9)	0.0046 (9)
C2	0.0299 (12)	0.0351 (13)	0.0253 (11)	0.0078 (9)	0.0005 (9)	−0.0033 (9)
C21A	0.058 (6)	0.056 (6)	0.022 (3)	0.007 (4)	−0.007 (3)	−0.010 (3)
C21B	0.016 (9)	0.026 (12)	0.037 (13)	0.007 (7)	0.009 (8)	0.000 (8)
O2	0.083 (7)	0.057 (6)	0.054 (5)	−0.016 (5)	−0.018 (5)	−0.021 (4)
C3	0.0274 (11)	0.0323 (12)	0.0322 (12)	0.0057 (9)	0.0034 (9)	−0.0021 (9)
C31A	0.033 (5)	0.039 (5)	0.060 (7)	−0.003 (3)	0.012 (4)	0.002 (4)
C31B	0.026 (12)	0.034 (14)	0.020 (11)	0.014 (11)	−0.002 (8)	0.002 (8)
O3	0.053 (5)	0.062 (6)	0.073 (6)	−0.029 (4)	0.004 (5)	−0.017 (5)

Geometric parameters (Å, º)

C11—O1	1.440 (3)	C21A—H21C	0.9800
C11—H11A	0.9800	C21B—O2	1.24 (4)
C11—H11B	0.9800	C21B—H21D	0.9500
C11—H11C	0.9800	C3—C31B	1.37 (6)
O1—C1	1.389 (3)	C3—C1^i	1.403 (3)

C1—C2	1.396 (4)	C3—C31A	1.54 (2)
C1—C3ⁱ	1.403 (3)	C31A—H31A	0.9800
C2—C21B	1.39 (4)	C31A—H31B	0.9800
C2—C3	1.402 (3)	C31A—H31C	0.9800
C2—C21A	1.538 (15)	C31B—O3	1.19 (5)
C21A—H21A	0.9800	C31B—H31D	0.9500
C21A—H21B	0.9800		

O1—C11—H11A	109.5	H21A—C21A—H21C	109.5
O1—C11—H11B	109.5	H21B—C21A—H21C	109.5
H11A—C11—H11B	109.5	O2—C21B—C2	128 (3)
O1—C11—H11C	109.5	O2—C21B—H21D	115.8
H11A—C11—H11C	109.5	C2—C21B—H21D	115.8
H11B—C11—H11C	109.5	C31B—C3—C2	121.3 (12)
C1—O1—C11	112.30 (18)	C31B—C3—C1ⁱ	120.1 (12)
O1—C1—C2	118.7 (2)	C2—C3—C1ⁱ	118.7 (2)
O1—C1—C3ⁱ	118.7 (2)	C2—C3—C31A	121.9 (6)
C2—C1—C3ⁱ	122.6 (2)	C1ⁱ—C3—C31A	119.4 (6)
C21B—C2—C1	121.2 (12)	C3—C31A—H31A	109.5
C21B—C2—C3	120.1 (12)	C3—C31A—H31B	109.5
C1—C2—C3	118.7 (2)	H31A—C31A—H31B	109.5
C1—C2—C21A	119.8 (6)	C3—C31A—H31C	109.5
C3—C2—C21A	121.5 (6)	H31A—C31A—H31C	109.5
C2—C21A—H21A	109.5	H31B—C31A—H31C	109.5
C2—C21A—H21B	109.5	O3—C31B—C3	129 (3)
H21A—C21A—H21B	109.5	O3—C31B—H31D	115.6
C2—C21A—H21C	109.5	C3—C31B—H31D	115.6

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C3/C1^v–C3^v benzene ring [symmetry code: (v) = -*x* + 1, -*y* + 1, -*z* + 1].

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C21*A*—H21*C*···O1ⁱⁱ	0.98	2.66	3.506 (15)	144
C11—H11*B*···O2ⁱⁱⁱ	0.98	2.71	3.195 (9)	111
C11—H11*A*···O3^{iv}	0.98	2.42	2.788 (9)	102
C31*A*—H31*C*···*Cg*1ⁱⁱ	0.98	2.71	3.48 (2)	138
C31*A*—H31*C*···*Cg*1^v	0.98	2.71	3.48 (2)	138

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) −*x*+2, −*y*+1, −*z*+2; (iv) −*x*+2, *y*−1/2, −*z*+3/2; (v) −*x*+2, −*y*+1, −*z*+1.